3.3 Use of the JPL Electronic Nose to Detect Leaks and Spills in an Enclosed Environment

M.A. Ryan, M.L. Homer, H. Zhou, C.C. Pelletier, K. Manatt, A.D. Jewell, A. Kisor, A.V. Shevade, C.R. Lewis, C.J. Taylor, S.-P.S. Yen
Jet Propulsion Laboratory, California Institute of Technology, Pasadena CA 91109

B. H. Weiller
The Aerospace Corp, El Segundo CA

M. Blanco, W.A. Goddard III
Materials Simulation Center, California Institute of Technology, Pasadena CA 91105

mryan@jpl.nasa.gov

Abstract: *An electronic nose to be used as an air quality monitor in human habitats in space has been developed at the Jet Propulsion Laboratory. This device is capable of detecting, identifying and quantifying several organic and inorganic chemical species which might be present as contaminants in spacecraft air. The complete portable device, including sensors, electronics, and software for data analysis, has been extensively tested.*

Keywords: chemical sensors; electronic nose; environmental monitoring; air quality monitor

Introduction

The Jet Propulsion Laboratory electronic nose (JPL ENose) is an autonomous, miniature device developed for use as an air quality monitor in human habitats in space [1,2]. This device is under development at JPL, where it has been taken from initial work at California Institute of Technology [3] in developing polymer-carbon black composite sensors to a fully operational device capable of identifying and quantifying 27 organic and inorganic chemical species that may be present in recycled air in spacecraft [1,4]. The JPL ENose detects target compounds at concentrations related to their 24-h spacecraft maximum allowable concentrations (SMACs), exposure levels set by NASA. The JPL ENose First-Generation device was successfully demonstrated in a six-day flight experiment on Space Shuttle flight STS-95 in 1998 [1,2,4]. The Second Generation ENose, developed from 1998 to 2003, focused on sensor and sensing array optimization [4,5], developing a molecular model of sensor response [6], and on further development of the hardware. The resulting device, shown in Figure 1, was trained to detect, identify and quantify 24 chemical species, which might be released through a leak or a spill in a spacecraft crew cabin. It has been ground-tested extensively, and includes data analysis software for real-time event detection.

In preparation for an upcoming, long-term (six month) technology demonstration aboard the international space station (ISS), the JPL ENose team is developing a Third Generation ENose. In this work, the capabilities of the JPL ENose are being expanded. Concurrently, the processes, tools and analyses which influence all aspects of development of the device are also being expanded.

For Generations One and Two, the analyte set focused on organic compounds such as common solvents along with a few selected inorganic compounds, ammonia, water and hydrazine. For the ISS technology demonstration two inorganic species have been added to the analyte set, mercury and sulfur dioxide. To accommodate these inorganic species, the sensor array will incorporate a hybrid sensing array approach, including both new sensing materials and new sensing platforms incorporating microhotplate sensor substrates. Initial approaches to materials selection for these analytes have been determined using models of sensor-analyte response. Predictive models will also be used to complement array training for additional software analyses including chemical family identification and identification of unknown analytes. Array analysis will be included on the ENose control computer and event analysis will be available within 15-30 minutes of event onset.

Electronic Noses

Traditional chemical sensors are designed to detect specific chemical species through unique interactions between sensing material and target species. Array-based sensing uses weakly specific sensors in which the pattern and magnitude of response are used to identify and quantify the presence of contaminants. The sensors used in the JPL ENose are conductometric chemical sensors which change resistance when the composition of its environment changes.

Electronic noses can be configured to respond to a broad range of compounds, and so they have been proposed for many applications, including both space and terrestrial environments. In space, chemical sensor arrays may be used for atmospheric and fluid studies on planetary surfaces and for monitoring air and water quality in human habitats. Terrestrial uses include such diverse applications as process control in the food and beverage industry, diagnosis of diseases from breath and body odor analysis and environmental monitoring for the presence of contaminants and toxins in air [7].

The JPL ENose is being developed for NASA to provide real-time, continuous air quality monitoring in human habitats, such as in crew vehicles (the Space Shuttle or the new Crew Exploration Vehicle now under development by NASA), in the International Space Station and in future lunar or martian surface habitats. Today, there is no real-time air quality monitoring in the International Space Station. Air quality is determined anecdotally by crew members' reports, and is measured by collecting samples for return to a ground laboratory for analysis using analytical instruments such as gas chromatography/mass spectrometry (GC/MS) or gas chromatography/ion mobility spectrometry (GC/IMS).

A real-time air quality monitor is envisioned to be used as an incident monitor, and would not take the place of an on-board analytical instrument such as GC/MS. Analytical instruments would be used regularly but not continuously to develop a complete description of the constituents of the breathing environment. An incident monitor such as the electronic nose is designed to monitor for changes caused by leaks, spills, or incipient fires between more detailed analysis [1,2]. It would run continuously in order to notify the crew of the presence of chemical species that are approaching dangerous levels so remedial action could be taken, or, in a fully automated system, remediation would be part of an automated environmental monitoring and control system [5,8,].

The JPL ENose

The JPL ENose is a complete, autonomous instrument composed of five basic parts: thirty-two conductometric chemical sensors; electronics designed to operate the device and to acquire and store data; fluid flow system, including a pump and filter system to bring air into the sensing chamber and to provide cleaned air for baselining, and a flow system designed to provide air in turbulent flow; the data analysis system, consisting of software where the training library designed to identify and quantify compounds resides; and a computer, which controls the device operation, acquires and stores data, processes the data, and provides a read-out of results.

The first-generation ENose, built for the 1998 flight experiment, occupied a volume of ~2000 cm^3, has a mass ~1.5 kg, and used 1.5 W average power (3 W peak), including the operating computer (HP 200 LX) [1,2]. The second-generation ENose (Figure 1) has the same functions as the first-generation device, but has been miniaturized to occupy less than 1000 cm^3 with a mass ~800 g, not including the operating computer. The power requirements of the 2nd-generation ENose are similar to those of the 1st 1st generation device. The body and flow system of the 2nd-generation device are made from a single block of hard-anodized aluminum; this design was chosen to eliminate fittings and to ensure that there are no leaks in the flow system. The 3rd generation JPL ENose uses the basic sensing unit developed as the second generation device; it also includes an ISS interface unit, which conforms to electrical, data telemetry, display and data storage requirements for ISS.

Figure 1: The Second Generation JPL ENose.

Sensors and the Sensing Array

Sensors: The majority of sensors used in the JPL ENose are conductometric, polymer-carbon black composite films. Sensors are made by solvent casting polymer-carbon black composite films onto screen-printed Pd-Au electrodes on a ceramic substrate. The films are electronically conducting because of conductive pathways formed by the carbon black in the polymer matrix [9].

Responses in the sensors are read as changes in direct current (DC) resistance. A baseline resistance is established for each sensor, and changes in that resistance indicate a change in the vapor constituents of the environment. The mechanism of response in polymer-carbon black composite sensing films is, at its simplest level, based on swelling in the film. Vapors in the environment partition into the film, causing the film to swell, which disrupts conductive pathways in the film by pushing carbon particles apart, and the electronic resistance in the film increases [1-3,5,10]. This change in resistance is measured and is used to construct the pattern of response across the sensing array (the "fingerprint or signature"), shown in Figure 2, which is analyzed using pattern matching software developed for the task. Elucidation of mechanisms of sensor response and of the chemical and physical characteristics that govern them that are the focus of the molecular modeling work underway at JPL [5,6].

At small swellings, the film returns fully to its initial unswollen state after the vapor source is removed, and the film resistance on each array element returns to (or very near to) its original value. Reversibility has been demonstrated for the polymer composite films used in our arrays for many thousands of vapor exposures, in room air and CO_2 background at various relative humidities and temperatures, for a diverse set of odors and polymers [1,10,11].

Inorganic Analytes: Inorganic species such as elemental mercury and SO_2 do not induce significant resistance

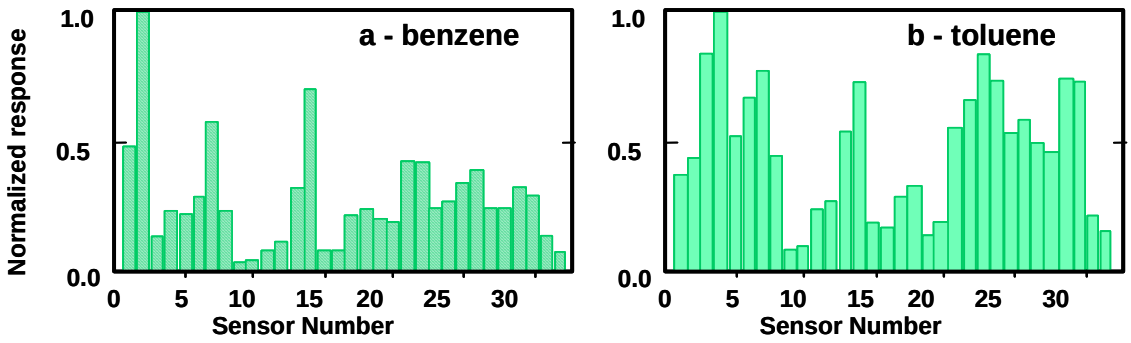

Figure 2: The pattern of response across the array in the 1st generation JPL ENose for benzene (a) and toluene (b). Sensor numbers refer to positions in the 1st generation array [1,2].

changes in the polymer-carbon composite sensors that have been used in earlier JPL ENoses. In order to add these analytes to our target species, it has been necessary to investigate alternative materials which will be added to the polymer-carbon composite sensors in the array.

SO_2 sensors will be developed using polymer-carbon black composites, which may be heated for regeneration. Modeling has shown that amine containing polymers may respond significantly to the presence of SO_2. Polymers under investigation are derivatives of linear and cross-linked poly-4-vinyl pyridine and vinyl benzyl chloride functionalized with various free-amine containing substituents.

Mercury is well known to form an amalgam with metallic films, such as gold or platinum, and several conductometric mercury sensors based on thin gold films have been reported and used. There are also organic materials that will bind with mercury. The focus of our efforts in this arena has been two-fold: developing a model of interaction between mercury and organic functionalities to predict whether polymer-based sensors will respond to mercury, and developing sensor materials and substrates that can use thin metallic films and can be regenerated. Microhotplate sensors from Aerospace Corporation [12] will be included in the 3rd generation JPL ENose to provide heatable platforms for sensor regeneration.

The Sensing Array: The sensing array used in the JPL ENose is a 32-element array made up of four substrates, each with eight sensors. Sensors made from 16 materials are deposited on these substrates. To obtain distinctive patterns across the array, materials for the 2nd-generation ENose were selected to provide a variety of chemical functionalities and interactions with the selected analytes, to ensure that fingerprints of response to each analyte are distinct [1]. Array selection used statistical tools to confirm that data analysis algorithms developed for the JPL ENose could distinguish among analytes of similar chemical structure.

Polymer selection depends on the suite of target compounds. If the target compounds represent a broad distribution of chemical functionalities, as for the JPL ENose, then a broad distribution of polymers will be necessary. The same set of polymers will distinguish compounds of very similar structures, isomers and enantiomers [13], as well as compounds of very different chemical structures, for instance propanol from benzene [1,2]. Figures 2a and 2b show that patterns for 30 parts-per-million of benzene and toluene are significantly different using the 32-sensor array, even though the analytes are structurally and chemically similar.

Effect of Environmental Conditions on Sensors

As with most chemical sensors, local conditions can have a significant effect on the response of polymer-carbon black composite films used as sensors. Whereas changes in humidity, temperature, and pressure tend to occur on a relatively slow time scale and so can be ignored if the device is used to monitor for changes over the previous few minutes, we have designed the JPL ENose to be able to look back over long periods (several hours) to determine whether there is evidence of a slow buildup of target compounds. On this time scale, changes in environmental conditions can obscure small changes in sensor response, because the sensors are very sensitive to changes in relative humidity of 1% or less and temperature changes of ~0.2°C. To diminish the effect of local temperature variations, the sensor substrates used in the JPL ENose are heated to ~4°C above the ambient temperature, and response to each target compound as a function of temperature has been characterized. Humidity is measured independently of the polymer-carbon black composite sensors and taken into account in data analysis through empirically determined algorithms, which describe the effect of humidity on each analyte in each polymer.

To distinguish between slow changes in sensor resistance caused by a slow leak of a target compound and that caused by baseline drift, a protocol for baselining was included in the ENose using air cleaned through a carbon filter at set intervals, then analyzing the virtual peak formed when the flow switches back to ambient air. If there is no change in the magnitude or fingerprint of the virtual peak over time, the air is considered to be unchanged and safe [1,2].

Data Analysis

The primary constraint in data analysis software development was the requirement that gas events of single or mixed gases from the target compounds be identified correctly and quantified accurately. In addition, three conflicting conditions were found in the data expected for air quality monitoring: a large number of target compounds, some of which are of very similar chemical structure (e.g., benzene and toluene); low target concentrations with nonlinear responses for some sensors at low concentrations; and single gases and mixtures.

To address these considerations, we have designed an automated routine to identify and quantify a gas event using an algorithm based on Levenberg-Marquart nonlinear least squares fitting (LM-NLS) [1,2,14,15]. Several other pattern recognition approaches were considered before LM-NLS was selected [15].

In the first-generation ENose, the success rate for identification and quantification was 85%. This success rate takes account of false positives and negatives as well as incorrect identification and/or quantification [1,2]. Further work is improving this rate.

Conclusions

The device developed as the second-generation ENose at JPL has been tested for its ability to respond to the compounds in Table I and is ready to operate as an autonomous device. Work continues in developing a model of sensor-analyte interaction to optimize selection of materials for a sensing array as well as for possible future use to identify array responses from untrained-for compounds.

Future application of the JPL ENose in space habitat or in planetary exploration will depend on NASA's needs, but eventual deployment of the ENose as one part of a fully automated environmental monitoring and control system is envisioned. In this scenario, activities such as remediation of spills and leaks would be actuated through a logic system and would be done robotically.

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